

Soft X-ray Emission Spectra of Crystalline Carbon Nitride Deposited by Electron Cyclotron Resonance (ECR) Sputtering

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INTRODUCTION

Carbon nitrides, especially β -C₃N₄, have been theoretically predicted by Cohen et al. [1-3] to be as hard as or even harder than diamond. This has stimulated many material scientists to try to deposit crystalline carbon nitride films by various methods. The characterization of carbon nitrides and investigation of their electronic structure have also become important in understanding how atomic bonding affects the calculated hardness. However, most experimental work on characterization has been done using electron diffraction or transmission electron microscopy (TEM) for identifying carbon nitride crystals; few x-ray spectroscopic studies have been done for electronic structure analysis because of the difficulty of obtaining crystalline films with sufficient crystalline purity for x-ray spectroscopy.

Recently, Tani et al.[4] succeeded in depositing high-purity crystalline carbon nitride films using electron-cyclotron-resonance (ECR) plasma sputtering methods. The crystal structure of these ECR-deposited carbon nitride films was confirmed by x-ray diffraction (XRD) and several chemical stoichiometric analysis methods to consist mainly of α - and β -C₃N₄ crystals, which may be spectroscopically high-purity crystalline films. We therefore measured high-resolution soft x-ray emission spectra of these ECR-deposited carbon nitride films to obtain information about the electronic structure of the carbon nitride crystals. In this paper, we describe the high-resolution C *K* and N *K* x-ray emission spectra, including selectively-excited and absorption spectra, of these ECR-deposited carbon nitride films and present information about their electronic structure.

EXPERIMENT

Carbon nitride films were deposited on Si(100) substrates by ECR sputtering, using a carbon target in a nitrogen atmosphere. The atomic ratio of nitrogen to carbon (N/C) was determined to be approximately 1.35, which agreed well with the stoichiometric composition of C₃N₄, according to x-ray photoelectron spectroscopy (XPS), heavy ion elastic recoil detection (ERD), and Rutherford backscattering (RBS). The crystal structure was analyzed by XRD, and a clearly observable XRD peak structure confirmed that the ECR-deposited carbon nitride films contained sufficient crystalline phases for x-ray spectroscopic measurements. Although an unknown diffraction peak was observed, the rest of the XRD pattern approximately agreed with the lattice constants theoretically predicted for α - or β -C₃N₄. The deposition process and chemical analysis of the ECR-deposited carbon nitride films are reported in detail elsewhere [4].

X-ray emission spectra in the C *K* and N *K* regions were measured using a grating x-ray spectrometer installed in beamline BL-8.0. Fluorescence-yield (FY) absorption spectra were also measured using this spectrometer. Total-electron-yield (TEY) absorption spectra were measured by monitoring the sample photocurrent in BL-6.3.2.

RESULTS AND DISCUSSION

Figure 1 shows (a) C *K* x-ray emission spectra of the ECR-deposited carbon nitride films and the reference carbon samples taken with 320-eV excitation and (b) the N *K* x-ray emission spectrum of the carbon nitride films with 430-eV excitation. In the C *K* spectra, the spectral shape of the carbon nitride consisted of a sharp main peak at 278.5 eV, a low-energy satellite at 266.5, and a high-energy-side tail near 282 eV. This spectral feature was completely different from those of the reference carbon samples. It is well known that the spectral shapes of graphite and diamond arise from sp^2 and sp^3 carbons respectively, and that the spectral shape of ion-beam-sputtered amorphous carbon may essentially arise from a mixture of sp^2 and sp^3 carbons. Therefore, the spectral shape of the carbon nitride suggests that carbon atoms in the film take up C-N bonding rather than sp^2 - or sp^3 -structured C-C bonding. The full width at half maximum (FWHM) of the symmetrical main peak of the carbon nitride is 2.8 eV, which is narrower than those of reference carbon compounds. This shows that the C2p electronic structure of the ECR-deposited carbon nitride films is more degenerated than that of the reference carbon samples. In the N *K* x-ray emission spectrum of the carbon nitride, two dominant peaks were observed at 392 eV and 388 eV.

In order to assign the spectral features of the C *K* and N *K* x-ray emission spectra of the carbon nitride, we tried to calculate C2p- and N2p-density of states (DOS) of carbon nitride clusters using discrete-variational (DV)-X α molecular orbital calculation methods [5]. A cluster model of $C_8N_{12}H_{28}$, which involves one unit cell structure of β - C_3N_4 , was used for the calculations. The C2p-DOS consists of three segments: the main segment is due to C2p, the low-energy segment is hybridized C2p-N2s, and the high-energy small segment is hybridized C2p-N2p. The N2p-DOS consists of roughly two segments: the high-energy segment is due to N2p and the low-energy segment is due to hybridized N2p-C2p. Using the calculated DOS spectral shapes as an analogy, we may therefore assign the spectral features of the ECR-deposited carbon nitride films as follows: the main peak (A) was caused by C2p, the low-energy satellite (B) by the hybridized C2p-N2s, and the high-energy tail (C) by hybridized C2p-N2p in the C *K* x-ray emission spectrum, and the 392-eV peak may be assigned to N2p and the 388-eV peak to hybridized N2p-C2p in N *K*. It is also confirmed that chemical bonds in the ECR-deposited carbon nitride film should be C-N bonds.

Figure 2 shows the selectively-excited C *K* x-ray emission spectra of the ECR-deposited carbon nitride film. TEY and FY absorption spectra are also shown in the upper panel. The emission peak intensities of both the 278.5-eV main peak and the 266.5-eV low-energy satellite were enhanced in the 288.6-eV excitation. However, no significant peak shifts or new peak appearances were observed for other energy excitations. This therefore suggests that the band structure of C2p in the ECR-deposited carbon nitride films is fairly non-dispersive.

Figure 3 shows the selectively excited N *K* x-ray emission spectra and absorption spectra. The high-energy emission peak at 392 eV was enhanced in the case of 407.5-eV excitation tuned at the higher-energy absorption peak. In comparison, the low-energy emission peak at 388 eV was enhanced and a small peak appeared at 390 eV in the case of 399.5-eV excitation tuned at the lower-energy absorption peak. Aside from these emission peak intensity enhancements and the appearance of a small peak, no other significant peak shifting was observed. This indicates that the band structure of N2p may also be fairly non-dispersive.

CONCLUSION

High-resolution soft x-ray emission spectra of ECR-deposited crystalline carbon nitride films were measured in the C *K* and N *K* regions. From the DV-X α molecular orbital calculations, the spectral features of the C *K* and N *K* x-ray emission can be assigned to the C2p- and N2p-DOS in

the hybridized C-N bonds. The narrow spectral shape observed in the C K x-ray emission suggests that the carbon nitride films have a highly degenerated electronic structure in their C-N bonds. Selectively-excited x-ray emission spectral measurements indicate that the band structure of the carbon nitride films should be fairly non-dispersive. These results also confirm that soft x-ray emission spectroscopy is a useful method for characterizing carbon nitride films.

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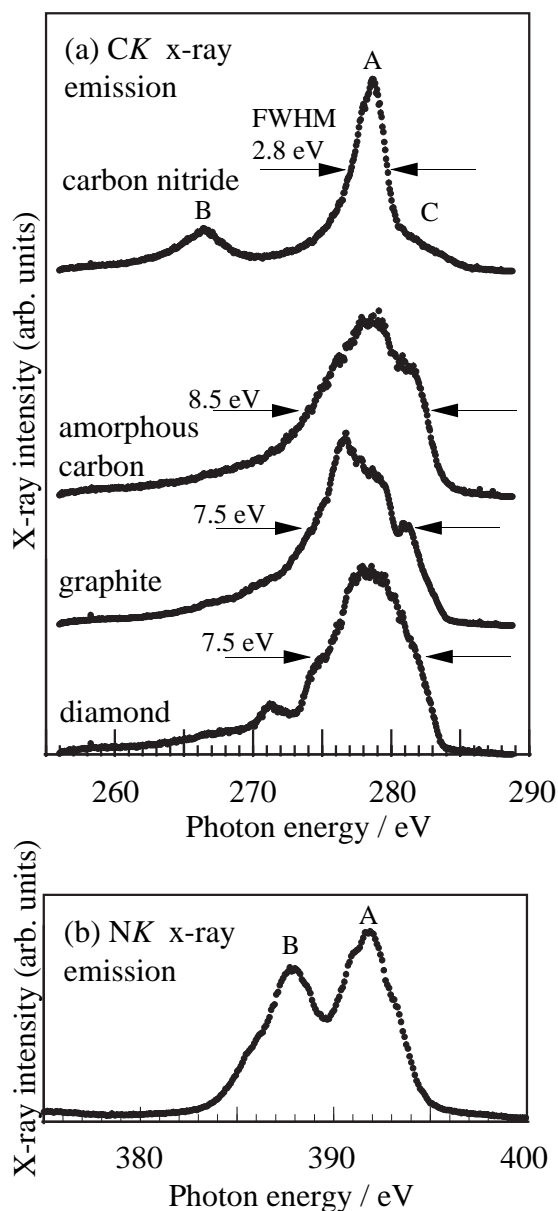


Figure 1 The upper panel (a) shows the C K x-ray emission spectra of the ECR-deposited carbon nitride film and reference carbon compounds such as ion-beam-sputtered amorphous carbon film, graphite powder, and diamond powder. The excitation energy was tuned to 320 eV. The lower panel (b) shows the N K x-ray emission spectrum of the carbon nitride obtained with 430-eV excitation.

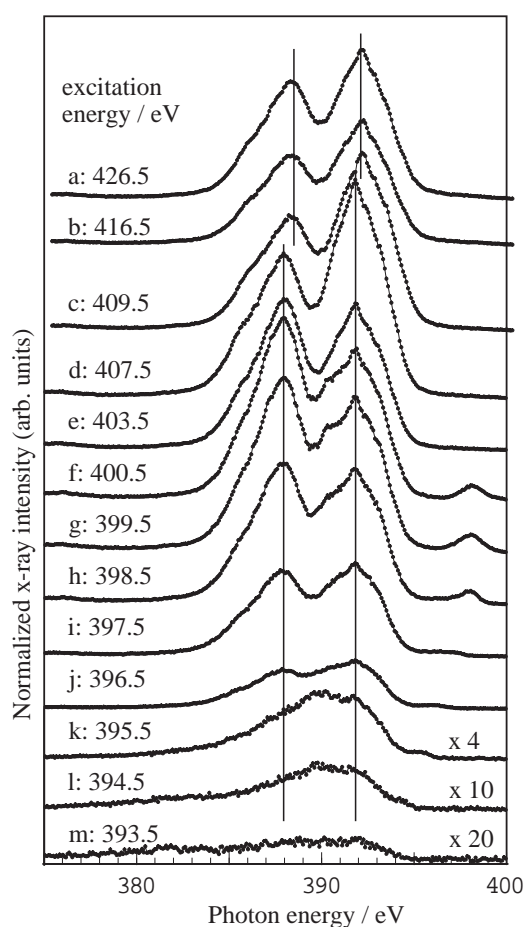
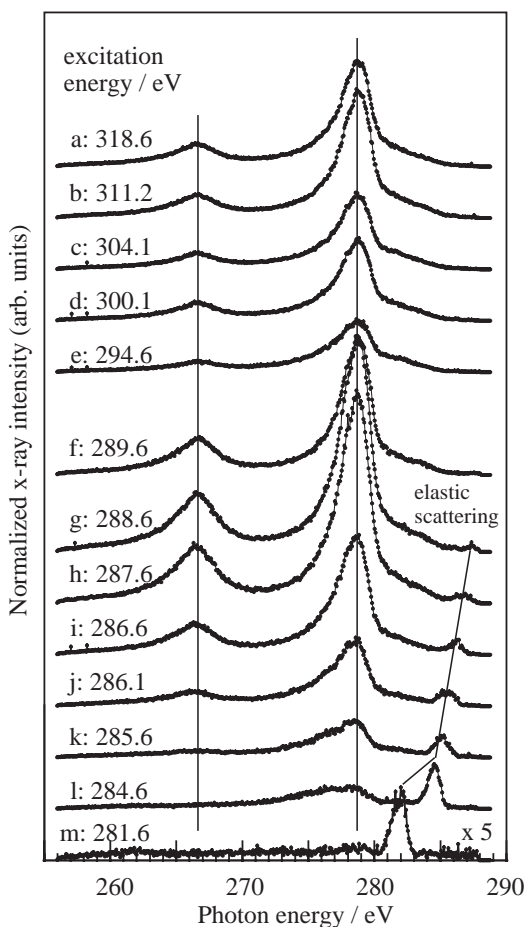
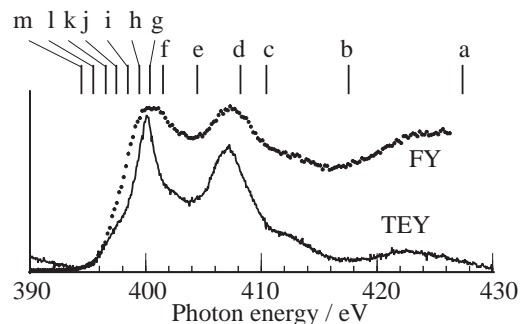
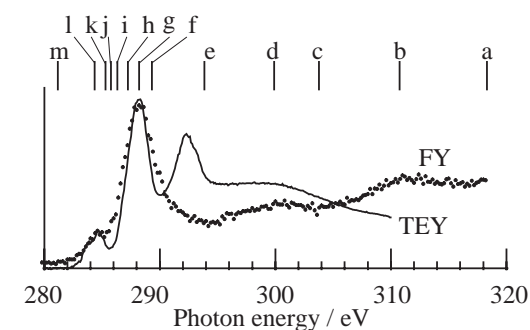


Figure 2 The lower panel shows the selectively-excited C K x-ray emission spectra of the ECR-deposited carbon nitride film. TEY and FY absorption spectra are shown in the upper panel. The excitation energy was tuned from 318.6 to 281.6 eV, as shown by “a” through “m” in the figure.

Figure 3 The lower panel shows the selectively-excited N K x-ray emission spectra of the ECR-deposited carbon nitride film. TEY and FY-absorption spectra are shown in the upper panel. The excitation energy was tuned from 426.5 to 393.5 eV, as shown by “a” through “m” in the figure.

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